Supporting Information

Design and performance evaluation of low-volatility low-viscosity absorbent for CO_2 capture

Ning Ma[1], Liu Yang[1], Zhenchang Fang[2], Kaijia Jiang[2], Xinling Li[1,3*], Zhen Huang[2,*]

[1]College of Smart Energy, Shanghai Jiao Tong University, China.

[2]Key Laboratory of Power Machinery and Engineering, Ministry of Education, Shanghai Jiao Tong University, China

[3]Institute of Eco-Chongming (IEC), Shanghai 202162, China

[*] Author for correspondence:

E-mail: lxl@sjtu.edu.cn (X.L.), z-huang@sjtu.edu.cn (Z.H.).

Number of pages: 11

Number of figures: 2

Number of tables:5

Text

Figure captions

Table captions

S1. Experimental Details

S1.1. Absorption Parameter Definition and Calculation

The CO_2 absorption rate can be calculated by the difference between the inlet and outlet CO_2 concentrations:

$$□_{□□□} = \frac{\frac{□_{□□□}(□_{□□} - □_{□□□})}{□_{□□□}□_0}}{\frac{□(1-□_{□□□})m_{□□□}}{□_0□_{□□□}}} \quad \text{(S1)}$$

where $□_{□□□}$ is the CO_2 absorption rate, mol CO_2/(min· kg); $□_{□□}$ and $□_{□□□}$ are the CO_2 concentrations at the inlet and outlet of the absorber, respectively; $m_{□□□}$ is the mass of the absorbent; □ is the ideal gas molar volume (22.4 L/mol); $□_{□□□}$ is the gas flow rate at the inlet. $□_{□□□}$ and $□_0$ are the atmospheric pressures under the actual and standard state, respectively, kPa; $□_{□□□}$ and $□_0$ are the temperatures under the actual and standard state, respectively, K.

The CO_2 absorption capacity can be obtained by integrating the absorption rate versus absorption time:

$$□□_{□□□} = \int_0^{□} □_{□□□}dt \quad \text{(S2)}$$

where $□□_{□□□}$ is the CO_2 absorption capacity, mol/kg, and □ is the absorption time, min.

S2. Calculation Parameter Description

S2.1. Quantum Computational Methods.

The molecular configurations, harmonic frequencies, and Gibbs free energies of the reactants, products, and transition states were optimized and calculated at the B3LYP/6-311++G(d, p) level using the density functional theory within the Gaussian 16W package[1,2]. The solvent effect was simulated using a universal implicit solvent model (SMD). Based on the results, the natural population analysis (NBO) charge distribution of the partial charges and electrostatic potential surfaces (EPS) were visualized with the GaussView 6.0.16 interface[3]. Calculation details can be found in the SI.

S2.2. Molecular Dynamics Simulation.

In MS 2023, the Forcite model is used to calculate hydrogen bond, van der Waals (vdW) solubility, and electrostatic solubility. The COMPASS III force field (Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies) is employed for simulating chemicals, a widely applied force field in molecular dynamics. After three optimizations (Dmol3 geometric optimization, Forcite geometric optimization, and NVT dynamic simulation for 100 ps), molecular interactions (hydrogen bond strength) and solubility parameters are elucidated using molecular dynamics simulations at 313K. Electrostatics are based on Ewald summation, and van der Waals forces are based on atomic calculations. The hydrogen bond is thought to exist between A and H if the distance |A-H| < 2.7 Å and the angle D-H-A > 120°. The hydrogen bond calculation results were taken as the average of 200 frames.

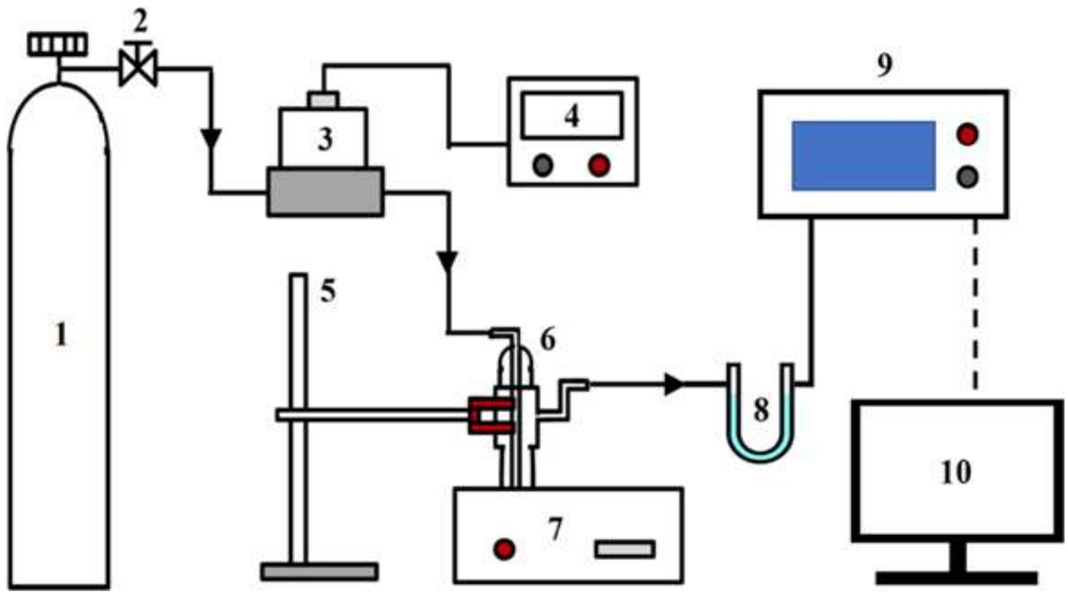

Fig S1. Schematic diagram of the CO_2 bubbling absorption experimental setup

1. Air intake cylinder; 2. Pressure reducing valve; 3. Mass flow controller; 4. flow rate indicator; 5. iron frame platform; 6. Bubbler; 7. Digital display constant temperature water bath; 8. drying device; 9. CO_2 concentration detector; 10. Data storage and processing equipment

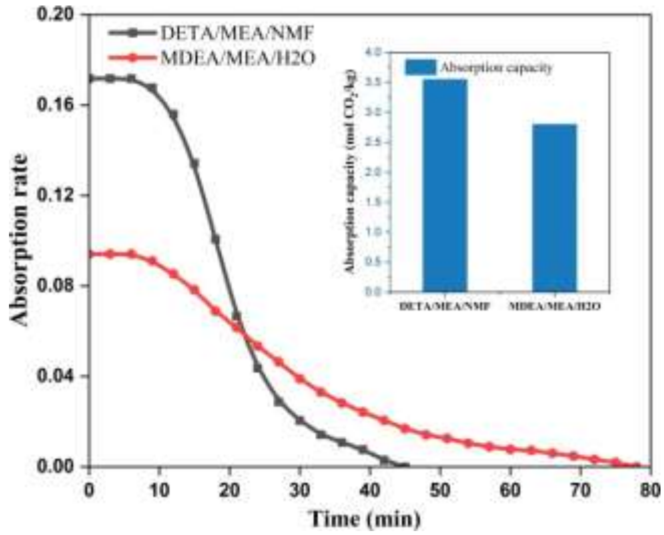

Fig S2. Comparison of absorption performance of DETA/MEA/NMF and MDEA/MEA/H_2O. ($C_{total\ amine}$: 5 M; $V_{solution}$: 25 mL; $T_{absorption}$: 313.15 K; $Q_{10\%}CO_2$:1L/min)

Table S1 Simulation analysis of hydrogen bonds formed and electrostatic solubility of MEA, MEA-CO_2 products in different solvents.

Absorbent name	Molecular number ratio	Hydrogen bond numbers	Average Hydrogen bond Length (A)	Electrostatic solubility
MEA-EG	MEA : EG = 100 : 251	780	2.021	30.23
MEA carbamate-EG	MEA carbamate : $MEAH^+$: EG = 50 : 50 : 251	1071	2.010	47.24
MEA-carbamic acid-EG	MEA-carbamic acid : EG = 100 : 251	852	2.008	28.00
MEA- NMF	MEA : NMF = 100 : 240	454	2.207	22.07
MEA carbamate-NMF	MEA carbamate : $MEAH^+$: NMF = 50 : 50 : 240	696	2.081	42.73
MEA-carbamic acid-NMF	MEA-carbamic acid : NMF = 100 : 240	542	2.117	21.61
MEA- DMSO	MEA : DMSO = 100 : 197	213	2.211	14.53
MEA carbamate-DMSO	MEA carbamate : $MEAH^+$: DMSO = 50 : 50 : 197	445	2.028	39.00
MEA-carbamic acid-DMSO	MEA-carbamic acid : DMSO = 100 : 197	299	2.088	15.65
MEA- DMF	MEA : DMF = 100 : 181	231	2.165	18.07
MEA carbamate-DMF	MEA carbamate : $MEAH^+$: DMF = 50 : 50 : 181	421	2.002	42.06
MEA-carbamic acid-DMF	MEA-carbamic acid : DMF = 100 : 181	295	2.008	19.15
MEA- NMP	MEA : NMP = 100 : 145	216	2.166	15.22
MEA carbamate-NMP	MEA carbamate : $MEAH^+$: NMP = 50 : 50 : 145	430	2.005	40.11

MEA-carbamic acid-NMP	MEA-carbamic acid : NMP = 100 : 145	290	2.017	16.65
MEA- EGME	MEA : EGME = 100 : 178	450	2.103	21.59
MEA carbamate-EGME	MEA carbamate : $MEAH^+$: EGME = 50 : 50 : 178	688	2.017	43.65
MEA-carbamic acid-EGME	MEA-carbamic acid : EGME = 100 : 178	523	2.048	20.91
MEA-BUTANOL	MEA : BUTANOL = 100 : 153	372	2.030	20.86
MEA carbamate-BUTANOL	MEA carbamate : $MEAH^+$: BUTANOL = 50 : 50 : 153	619	1.983	44.52
MEA-carbamic acid-BUTANOL	MEA-carbamic acid : BUTANOL = 100 : 153	445	1.987	20.14
MEA-Cyclohexanol	MEA : Cyclohexanol = 100 : 132	317	2.044	18.07
MEA carbamate-Cyclohexanol	MEA carbamate : $MEAH^+$: Cyclohexanol = 50 : 50 : 132	581	1.990	41.91
MEA-carbamic acid-Cyclohexanol	MEA-carbamic acid : Cyclohexanol = 100 : 132	396	1.992	17.88
MEA-ISOBUTANOL	MEA : ISOBUTANOL = 100 : 152	359	2.021	20.15
MEA carbamate-ISOBUTANOL	MEA carbamate : $MEAH^+$: ISOBUTANOL = 50 : 50 : 152	608	1.980	44.59
MEA-carbamic acid-ISOBUTANOL	MEA-carbamic acid : ISOBUTANOL = 100 : 152	427	1.982	19.55

Table S2. The values of reaction rate constants (k) and the equilibrium constant (K) were estimated based on the activation free energy (Ea, kJ/mol) and the gibbs free energy change (ΔG, kJ/mol)

	Ea	ΔG	k	K
MEA1	5.616732	-19.1827	6.434E+11	2.304E+03
MEA2	1.872244	-27.1422	2.916E+12	5.725E+04
DETA1	3.930636	-23.3312	1.271E+12	1.230E+04
DETA2	0.919188	-30.7375	4.285E+12	2.443E+05

Table S3. Absorption capacity and solution viscosity of the DETA/MEA/NMF at different temperatures

Absorption temperature, K	Absorption capacity, mol CO_2/kg	Viscosity of saturated solution, mPa· s
293	3.84	220.61
303	3.75	123.34
313	3.55	60.48
323	3.40	36.34
333	3.20	20.31

Table S4. vapor pressures, boiling points and specific heat capacities of the organic solvents[4]

Organic solvents	Vapor pressure at 373K, kPa	Boiling point at 1 atm, K	Specific heat capacity, kJ/(kg· K)
DMSO	4.99	462	1.95
EG	2.15	468	2.35
DMF	21.12	426	2.14
NMF	3.00	456	2.07
Isobutanol	75.62	381	2.39
Butanol	51.56	390	2.33
EGME	44.35	398	2.20
NMP	3.34	475	1.77
Cyclohexanol	10.52	434	2.15

Table S5. Mass loss of MEA/H_2O and DETA/MEA/NMF at different temperatures over 24 hours

Temperature, K	Time, hour	Mass loss, g	
		MEA/H_2O	DETA/MEA/NMF
293	6	0.0070	0.0025
293	12	0.0064	0.0037
293	24	0.0117	0.0077
353	6	0.0662	0.0274
353	12	0.0794	0.0300
353	24	0.1983	0.0633

REFERENCES

(1) Frisch, M. J. Gaussian 16 Rev. C.01, 2016.

(2) Yu, Y.; Shen, Y.; Zhou, X.; Liu, F.; Zhang, S.; Lu, S.; Ye, J.; Li, S.; Chen, J.; Li, W. Relationship between Tertiary Amine’s Physical Property and Biphasic Solvent’s CO2 Absorption Performance: Quantum Calculation and Experimental Demonstration. *Chem. Eng. J.* **2022**, *428*, 131241. https://doi.org/10.1016/j.cej.2021.131241.

(3) Al-Marri, M. J.; Khader, M. M.; Giannelis, E. P.; Shibl, M. F. Optimization of Selection of Chain Amine Scrubbers for CO2 Capture. *J. Mol. Model.* **2014**, *20* (12), 2518. https://doi.org/10.1007/s00894-014-2518-8.

(4) Dykyj, J.; Svoboda, J.; Wilhoit, R. C.; Frenkel, M.; Hall, K. R.; Hall, K. R. Organic Compounds, C1 to C57. Part 1: Datasheet from Landolt-Börnstein - Group IV Physical Chemistry · Volume 20B: “Vapor Pressure and Antoine Constants for Oxygen Containing Organic Compounds” in SpringerMaterials (Https://Doi.Org/10.1007/10688583_3). https://doi.org/10.1007/10688583_3.